

# PATENT SPECIFICATION

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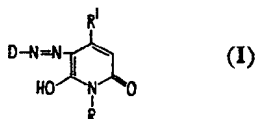


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## (54) AZO DYESTUFFS, THEIR MANUFACTURE AND USE

(71) We, CIBA-GEIGY A.G. a Swiss Body Corporate of Basle, Switzerland do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention provides azo dyestuffs which contain an acid substituent which confers solubility in water, and are of the formula



wherein D denotes the radical of a diazo component, R denotes an optionally substituted alkyl or cyclohexyl radical and R' denotes an optionally substituted alkyl or aryl radical. The diazo radical is a carbocyclic or heterocyclic aromatic radical which can itself contain an azo group, or which is derived from a compound of, for example, the anthraquinone, nitroaryl, phthalocyanine or stilbene series. In particular, the diazo radical is a radical of the benzene or naphthalene series.

The azo dyestuffs according to the present invention contain groups which confer solubility in water, such as, for example sulphonic acid groups or carboxyl groups. Above all, the compounds can contain one or more than one fibre reactive radical, in particular cyclic fibre-reactive radicals, such as triazine, pyrimidine and cyclobutane radicals, and especially a halogenotriazine radical, in the molecule. In addition to being substituted by groups which confer solubility in water, the azo compounds can be substituted by further atoms or groups of atoms, both in the radical of the diazo component and in the radicals R and R', for example halogen atoms and hydroxyl, amino, alkyl, aryl, alkoxy, aryloxy, acylamino, nitrile, acyl, alkoxy-carboxyl, acyloxy or nitro groups. If the radical of the diazo component contains in the ortho-position to the azo bridge, a metal complex-forming group, such as for example, a hydroxyl, amino or carboxyl group or an alkoxy group, such as, for example, a methoxy group, the azo compounds in question can optionally be converted to their heavy metal (i.e. a metal having an atomic number from 23 to 29) complex compounds either before the introduction of fibre-reactive radicals or afterwards.

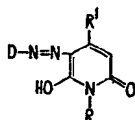
Possible complex-forming metals are, for example, iron, manganese, nickel, copper, cobalt and chromium. The heavy metal complexes can contain one or two molecules of azo dyestuff of the formula (1), joined to a metal atom (1:1- or 1:2-complexes). However, in 1:2-complexes one of the two ligand molecules can also be an azo compound

which is not of the formula (1), that is to say, for example, a compound of the azo benzene type which contains appropriate complex-forming groups.

Groupings capable of reacting with the hydroxyl groups of cellulose or with the amino groups of polyamides, with the formation of a covalent chemical bond, are appropriate fibre-reactive radicals. Such a grouping is, in particular, a low molecular weight (i.e. of 1 to 4 carbon atoms) alkanoyl or alkylsulphonyl radical substituted by a removable atom or a removable group, i.e. an atom or group which can be removed by reaction with the hydroxyl or amino groups of the fibre, a low molecular weight alkenoyl or alkenesulphonyl radical optionally substituted by a removable atom or a removable group, a carbocyclic or heterocyclic radical containing 4-, 5- or 6-membered rings which is substituted by a removable atom or a removable group and is bonded via a carbonyl or sulphonyl group, or a triazine or pyrimidine radical substituted by a removable atom or a removable group and directly bonded via a carbon atom, or a grouping containing such a radical. A six-membered heterocyclic radical with two or three ring nitrogen atoms which contains halogen atoms and is bonded via a  $\text{---NH---}$  group, in particular a chloro-1,3,5-triazine radical, is preferred as the fibre-reactive radical.

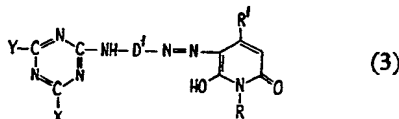
A possible coupling component is, in particular, the radical of a 1,4-dialkyl-6-hydroxypyrid-2-one.

The present invention relates, in particular, to compounds of the formula



wherein R and R' are alkyl radicals with at most 4 carbon atoms and wherein D denotes the radical of a diazo component of the benzene series.

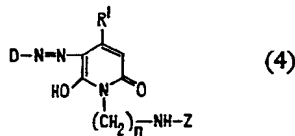
A special group of compounds according to the invention are those of the formula



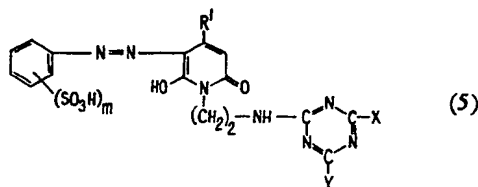
wherein D' is a sulphobenzene radical, X is a halogen atom and Y is a halogen atom or an amino, alkoxy, phenoxy, or mercapto radical. The benzene radical can also carry further substituents in addition to one or two sulphonic acid groups as already mentioned.

Particularly valuable compounds are those of the formula (3), wherein D' is a monosulphobenzene radical, in particular such a radical which contains no further substituents other than a sulphonic acid group, X is a halogen atom, Y is an aminobenzene (or aminonaphthalene)disulphonic acid radical, and R and R' are each a methyl or ethyl radical.

A further group of interesting compounds are those of the formula



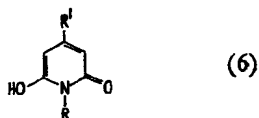
wherein D is the radical of a diazo component of the benzene or naphthalene series, in particular such a radical which contains substituents which confer solubility in water, R' is an alkyl or aryl radical, Z is a fibre-reactive radical, in particular a dihalogenotriazine radical or a monohalogenotriazine radical which contains an ammonium, amino, alkoxy, phenoxy or mercapto radical bonded to a carbon atom, and n is a positive integer, preferably between 1 and 4. Valuable compounds of this type are those of the formula



wherein X is a halogen atom, in particular a chlorine or bromine atom, Y is an amino-benzene (or aminonaphthalene)-sulphonic acid radical, R' is a low molecular weight alkyl radical, in particular a methyl radical, and m is 1 or 2.

The manufacture of the azo dyestuffs according to the present invention can be carried out by diazotisation of an amine of the formula: D—NH<sub>2</sub>, and coupling and, where appropriate, metallisation and/or acylation in order to introduce a metal and a fibre reactive radical, respectively.

The coupling is characterised in that a diazo component of an amine of formula D—NH<sub>2</sub>, in particular such a component of the benzene series, is coupled with a compound of the formula



wherein R and R' are as defined above, in particular alkyl radicals with 1 to 4 carbon atoms; the resulting azo dyestuff is optionally converted to a heavy metal complex by reaction with a heavy metal donor. The starting compounds are preferably diazo components which contain a fibre-reactive radical and a group which confers solubility in water. Possible coupling components for dyestuffs of the formula (4) are, in particular, 1,4-dialkyl-6-hydroxypyrid-2-ones.

The diazotisation can be carried out by methods which are in themselves known, for example by means of hydrochloric acid and sodium nitrite. The coupling with the pyridone can also be carried out according to methods which are in themselves known, in an acid to weakly alkaline medium.

The reaction with the heavy metal donor can be carried out according to customary methods, in various solvents, such as, for example, water, ethanol, formamide, glycol-ethers and pyridine, depending on the solubility of the components, optionally at elevated temperature, and in a weakly acid to alkaline medium.

As diazo components which can be employed for the manufacture of the compounds according to the invention, or the corresponding heavy metal complexes, the diazo compounds of the following amines may be mentioned:

Aniline,  
 1-Amino-4-chlorobenzene,  
 1-Amino-4-bromobenzene,  
 1-Amino-4-methylbenzene,  
 1-Amino-4-nitrobenzene,  
 1-Amino-4-cyanobenzene,  
 1-Amino-2,5-dicyanobenzene,  
 1-Amino-4-methylsulphonylbenzene,  
 1-Amino-4-alkoxycarbonylbenzene,  
 1-Amino-2,4-dichlorobenzene,  
 1-Amino-2,4-dibromobenzene,  
 1-Amino-2-methyl-4-chlorobenzene,  
 1-Amino-2-trifluoromethyl-4-chlorobenzene,  
 1-Amino-2-cyano-4-chlorobenzene,  
 1-Amino-2-methoxycarbonyl-4-chlorobenzene,  
 1-Amino-2-methoxycarbonyl-4-nitrobenzene,  
 1-Amino-2-chloro-4-cyanobenzene,  
 1-Amino-2-chloro-4-nitrobenzene,  
 1-Amino-2-bromo-4-nitrobenzene,  
 1-Amino-2-chloro-4-ethoxycarbonylbenzene,

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|----|--|--|----|
|    | 1-Amino-2-chloro-4-methylsulphonylbenzene,<br>1-Amino-2-methylsulphonyl-4-chlorobenzene,<br>1-Amino-2,4-dinitro-6-methylsulphonylbenzene,<br>1-Amino-2,4-dinitro-6-(2'-hydroxyethylsulphonyl)-benzene,<br>1-Amino-2,4-dinitro-6-(2'-chloroethylsulphonyl)-benzene,<br>1-Amino-2-methylsulphonyl-4-nitrobenzene,<br>1-Amino-4-methylsulphonyl-2-nitrobenzene,<br>1-Amino-2,4-dinitrobenzene,<br>1-Amino-2,4-dicyanobenzene,<br>1-Amino-2-cyano-4-methylsulphonylbenzene,<br>1-Amino-2,6-dichloro-4-cyanobenzene,<br>1-Amino-2,6-dichloro-4-nitrobenzene,<br>1-Amino-2,4-dicyano-6-chlorobenzene,<br>4-Aminobenzoic acid cyclohexyl ester,<br>1-Amino-2,4-dinitro-6-chlorobenzene and in particular<br>1-Amino-2-cyano-4-nitrobenzene,<br>1-1-Aminobenzene-2-, -3- or -4-sulphonamide, such as the<br>N-methyl- or N,N-dimethyl- or -diethylamide,<br>2-Aminonaphthalene-6-sulphonic acid-N, $\gamma$ -isopropoxypropylamide,<br>1-Aminobenzene-2-, -3- or -4-sulphonic acid-N, $\gamma$ -isopropoxy-propylamide,<br>1-Aminobenzene-2-, -3- or -4-sulphonic acid-N-isopropylamide,<br>1-Aminobenzene-2-, -3- or -4-sulphonic acid-N, $\gamma$ -methoxypropylamide,<br>1-Aminobenzene-2-, -3- or -4-sulphonic acid-N,N-bis- $\beta$ -hydroxyethyl-,amide,<br>1-Amino-4-chlorobenzene-2-sulphonamide,<br>and the N-substituted derivatives,<br>4-Aminoazobenzene,<br>3,2'-Dimethyl-4-aminoazobenzene,<br>2-Methyl-5-methoxy-4-aminoazobenzene,<br>4-Amino-2-nitroazobenzene,<br>2,5-Dimethoxy-4-aminoazobenzene,<br>4'-Methoxy-4-aminoazobenzene,<br>2-Methyl-4'-methoxy-4-aminoazobenzene,<br>3,6,4'-Trimethoxy-4-aminoazobenzene,<br>4'-Chloro-4-aminoazobenzene,<br>2'- or 3'-chloro-4-aminoazobenzene,<br>3-Nitro-4-amino-2',4'-dichloroazobenzene,<br>4-Aminoazobenzene-4'-sulphonamide,<br>1- or 2-Aminonaphthalene,<br>4-Methoxy-5-chloro-2-aminophenol,<br>6-Acetylamino-4-chloro-2-aminophenol,<br>6-Nitro-4-chloro-2-aminophenol,<br>6-Nitro-4-methyl-2-aminophenol,<br>3-Amino-4-hydroxy-acetophenone,<br>6-Nitro-4-acetylamino-2-aminophenol,<br>5-Nitro-3-amino-4-hydroxy-acetophenone,<br>2-Aminophenol-4-carboxylic acid amide,<br>4,6-Dichloro-2-aminophenol,<br>3,4,6-Trichloro-2-aminophenol,<br>4-Nitro-6-chloro-2-aminophenol,<br>6-Nitro- or 6-chloro-2-aminophenol-4-sulphonamide,<br>4-Nitro-2-aminophenol-5- or -6-sulphonamide,<br>2-Aminophenol-5-methylsulphone,<br>2-Aminophenol,<br>4- or 5-Nitro-2-aminophenol,<br>4- or 5-Chloro-2-aminophenol,<br>4,5-Dichloro-2-aminophenol,<br>4-Chloro-5-nitro-2-aminophenol,<br>2-Aminophenol-4- or -5-sulphonic acid,<br>3,4,6-Trichloroaminophenol,<br>4-Chloro-2-aminophenol-6-sulphonic acid,<br>6-Chloro-2-aminophenol-4-sulphonic acid,<br>4-Nitro-2-aminophenol-6-sulphonic acid,<br>6-Nitro-2-aminophenol-4-sulphonic acid,<br>2-Aminophenol-4,6-disulphonic acid,<br>4,6-Dinitro-2-aminophenol, |  |    |
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|----|---|----|
|    | 6-Acetylamino-2-aminophenol-4-sulphonic acid,                           |    |
|    | 4-Acetylamino-2-aminophenol-6-sulphonic acid,                           |    |
|    | 4-Methyl-2-aminophenol,   |    |
|    | 4-Methoxy-2-aminophenol,  |    |
| 5  | 2-Aminophenol-4-sulphonamide,   | 5  |
|    | 2-Aminophenol-4-sulphone-N- $\beta$ -hydroxyethylamide,                 |    |
|    | 2-Aminophenol-4-sulphone-N-methylamide,                                 |    |
|    | 2-Aminophenol-5-sulphonamide,   |    |
|    | 4-Chloro-2-aminophenol-5- or -6-sulphonamide,                           |    |
| 10 | 2-Aminophenol-4-sulphone-N,N-dimethylamide,                             | 10 |
|    | 2-Aminophenol-4-methylsulphone,   |    |
|    | 2-Aminophenol-4-ethylsulphone,  |    |
|    | 6-Acetylamino-4-nitro-2-aminophenol,                                    |    |
|    | 2-Aminophenol-4- $\beta$ -hydroxyethylsulphone,                         |    |
| 15 | Anthranilic acid,   | 15 |
|    | 2-Amino-3-naphthoic acid,   |    |
|    | 4- or 5-Chloroanthranilic acid,   |    |
|    | 4- or 5-Nitroanthranilic acid,  |    |
|    | 4- or 5-Acetylaminoanthranilic acid,                                    |    |
| 20 | 4- or 5-Sulphoanthranilic acid,   | 20 |
|    | Anthranilic acid-4-sulphonamide,  |    |
|    | Anthranilic acid-4- or -5- $\beta$ -hydroxyethylsulphone,               |    |
|    | Anthranilic acid-4- or -5-ethylsulphone,                                |    |
|    | 4-Chloro-2-aminophenol-5-sulphonic acid-N-methylamide,                  |    |
| 25 | 4- or 5-Benzoylaminoanthranilic acid,                                   | 25 |
|    | 2-Anisidine,  |    |
|    | 4- or 5-Chloro-2-anisidine,   |    |
|    | 4- or 5-Nitro-2-anisidine,  |    |
|    | 2-Anisidine-4- or -5-sulphonic acid,                                    |    |
| 30 | 2-Methoxy-5-methylaniline,  | 30 |
|    | 2,5-Dimethoxyaniline,   |    |
|    | 2-Anisidine-4- or -5- $\beta$ -hydroxyethylsulphone,                    |    |
|    | 2-Amino-1-naphthol-4,8-disulphonic acid,                                |    |
|    | 1-Amino-2-naphthol-4-sulphonic acid,                                    |    |
| 35 | 1-Amino-2-naphthol-4-sulphonamide,                                      | 35 |
|    | 6-Nitro-1-amino-2-naphthol-4-sulphonic acid,                            |    |
|    | 6-Acetylamino-1-amino-2-naphthol-4-sulphonic acid,                      |    |
|    | 4-(2',5'-Disulphophenylazo)-2-methoxy-5-methylaniline,                  |    |
|    | 4-(2',5'-Disulphophenylazo)-2,5-dimethoxyaniline,                       |    |
| 40 | 4-(2',5'-Disulphophenylazo)-2-methoxy-1-naphthylamino-6-sulphonic acid, | 40 |
|    | 4-(1',5'-Disulphonaphth-2'-ylazo)-2,5-dimethoxyaniline,                 |    |
|    | 4-(2',3'- or 4'-Sulphophenylazo)-2-methoxyaniline,                      |    |
|    | Dianisidine,  |    |
|    | Benzidine-3,3'-dicarboxylic acid,                                       |    |
| 45 | 4-(2',3'- or 4'-Sulphophenylazo)-2-methoxy-5-methylaniline,             | 45 |
|    | 4-(2',3'- or 4'-Sulphophenylazo)-2,5-dimethoxyaniline,                  |    |
|    | 4-(2',5'- or 3',5'-Disulphophenylazo)-2-methoxyaniline,                 |    |
|    | 4-(3',5'-Disulphophenylazo)-2-methoxy-5-methylaniline,                  |    |
|    | 4-(3',5'-Disulphophenylazo)-2,5-dimethoxyaniline,                       |    |
| 50 | 4-(2'-Carboxy-4'- or -5'-sulphophenylazo)-2-methoxyaniline,             | 50 |
|    | 4-(2'-Carboxy-4- or -5'-sulphophenylazo)-2,5-dimethoxyaniline,          |    |
|    | 4-(2'-Carboxy-4'- or -5'-sulphophenylazo)-2-methoxy-5-methylaniline,    |    |
|    | 4-(6',8'-Disulphonaphth-2'-ylazo)-2-methoxyaniline,                     |    |
|    | 4-(6',8'-Disulphonaphth-2'-ylazo)-2-methoxyaniline,                     |    |
| 55 | 4-(6',8'-Disulphonaphth-2'-ylazo)-2-methoxy-5-methoxyaniline,           | 55 |
|    | 4-(6',8'-Disulphonaphth-2'-ylazo)-2,5-dimethoxyaniline,                 |    |
|    | 4-Phenylazo-2-aminophenol.  |    |
|    | Metanilic acid,   |    |
|    | Sulphanilic acid,   |    |
| 60 | Orthanilic acid   | 60 |
|    | 1-Amino-4-methylbenzene-2-sulphonic acid,                               |    |
|    | Aniline-2,5-disulphonic acid,   |    |
|    | 2-Naphthylamine-1-sulphonic acid,                                       |    |
|    | 2-Naphthylamine-1,5-disulphonic acid,                                   |    |
| 65 | 2-Naphthylamine-4,8-disulphonic acid,                                   | 65 |

2-Naphthylamine-4,6,8- or -3,6,8-trisulphonic acid,  
 1-Amino-4-( $\beta$ -sulphatoethylsulphonyl)-benzene,  
 1-Amino-3-( $\beta$ -sulphatoethylsulphonyl)-benzene,  
 1-Amino-2-methoxy-4-( $\beta$ -sulphatoethylsulphonyl)-5-methyl-benzene,  
 1-Amino-4-( $\beta$ -sulphatoethylsulphonamido)-benzene,  
 1-Amino-4-( $\beta$ -hydroxyethylsulphonyl)-benzene,

As coupling components there may be mentioned:

1-Ethyl-4-methyl-6-hydroxypyridone(2),  
 1-( $\beta$ -Hydroxyethyl)-4-methyl-6-hydroxy-pyridone(2),  
 1-Methyl-4-phenyl-6-hydroxy-pyridone(2),  
 1-Butyl-4-methyl-6-hydroxy-pyridone(2),  
 1-Ethyl-4-hexyl-6-hydroxy-pyridone(2),  
 1-Isopropyl-4-methyl-6-hydroxy-pyridone(2),  
 1-Ethyl-4-phenyl-6-hydroxy-pyridone(2),  
 1,4-Dimethyl-6-hydroxy-pyridone(2),  
 1-( $\beta$ -Methoxyethyl)-4-methyl-6-hydroxy-pyridone(2),  
 1-Propyl-4-methyl-6-hydroxy-pyridone(2),  
 1-( $\beta$ -Aminoethyl)-4-methyl-6-hydroxypyridone(2).

Azo dyestuffs of the present invention, or the corresponding heavy metal complexes, which contain one or more fibre-reactive groups can be manufactured by employing diazo or coupling components which already contain fibre-reactive groups. However, in many cases it is also possible to introduce reactive groups subsequently into the azo compounds. Those compounds of formula (1) which contain a six-membered heterocyclic reactive radical bonded via an amino group, are of particular interest.

The introduction of the fibre-reactive radical is preferably effected by acylating appropriate aminoazo compounds or coupling components which contain an amino group which can be acylated, or appropriate diazo components, which, in addition to the amino group to be diazotised, contain a further amino group which can be acylated, or a group which can be converted to an amino group which can be acylated, for example by reduction or saponification, such as, for example, the nitro group or the acetyl amino group. The term "acylating" as used herein means reacting with a compound introducing a  $\text{—CO—R}_1$  group where  $\text{R}_1$  denotes an organic radical, such as a carboxylic acid halide or anhydride or a compound which reacts in a similar manner to such a halide or anhydride, for example halogenated heterocyclic compounds containing reactive halogen atoms e.g. halogenotriazines and halogenopyrimidines.

Appropriate diazo components which, as described above, are suitable for introducing a fibre-reactive radical, are, for example:

1,3-Diaminobenzene-4-sulphonic acid,  
 1,3-Diaminobenzene-4,6-disulphonic acid,  
 1,4-Diaminobenzene-2-sulphonic acid,  
 1,4-Diaminobenzene-2,5- or -2,6-disulphonic acid,  
 1-Amino-4-nitrobenzene,  
 1-Amino-2-chloro-4-nitrobenzene,  
 1,3-Diamino-4-methylbenzene-6-sulphonic acid,  
 6-Acetyl amino-4-chloro-2-aminophenol,  
 6-Nitro-4-methyl-2-aminophenol,  
 4-Nitro-2-aminophenol-6-sulphonic acid,  
 6-Acetyl amino-1-amino-2-naphthol-4-sulphonic acid,  
 as well as compounds already mentioned in the recitation of possible diazo components.

The coupling products, for example of the above-mentioned diazo components with appropriate pyridones are possible aminoazo compounds which can be introduced into the fibre-reactive radicals after the coupling.

The halides or anhydrides of organic acids which contain easily replaceable atoms or groups of atoms are, in particular, possible acylating agents which, in addition to the acylating radical, also contain a reactive radical.

As an acylating agent containing a fibre-reactive radical, the following may for example be mentioned:

Chloro- or bromoacetyl chloride,  
 $\beta$ -Chloro- or  $\beta$ -bromopropionyl chloride,  
 $\alpha,\beta$ -Dichloro- or  $\alpha,\beta$ -dibromopropionyl chloride,  
 Chloromaleic acid anhydride,  
 Carbylsulphate,  
 Acryloyl chloride,  
 $\beta$ -Chloro- or  $\beta$ -bromoacryloyl chloride,  
 $\alpha$ -Chloro- or  $\alpha$ -bromoacryloyl chloride,

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|    | $\alpha,\beta$ -Dichloro- or -dibromoacryloyl chloride,<br>Trichloroacryloyl chloride,<br>Chlorocrotonyl chloride,<br>Propiolic acid chloride,  |    |
| 5  | 3,5-Dinitro-4-chlorobenzene-sulphonic acid or -carboxylic acid chloride,<br>3-Nitro-4-chlorobenzene-sulphonic acid or -carboxylic acid chloride,<br>2,2,3,3-Tetrafluorocyclobutane-1-carboxylic acid chloride,<br>2,2,3,3-Tetrafluorocyclobutyl-acrylic acid chloride,<br>$\beta$ -Chloroethylsulphonyl-endomethylene-cyclohexanecarboxylic acid chloride,  | 5  |
| 10 | Acrylsulphonyl-endomethylene-cyclohexanecarboxylic acid chloride,<br>and, above all, heterocyclic acid halides and their derivatives, such as the<br>2-Chlorobenzoxazole carboxylic acid chlorides,<br>2-Chlorobenzthiazole carboxylic acid chlorides or -sulphonic acid chlorides, and, above<br>all, the following compounds possessing at least 2 nitrogen atoms as hetero-atoms in a<br>6-membered heterocyclic ring:   | 10 |
| 15 | 4,5-Dichloro-1-phenylpyridazonecarboxylic acid chloride or -sulphonic acid chloride,<br>4,5-Dichloropyridazonepropionic acid chloride,<br>1,4-Dichlorophthalazinecarboxylic acid chloride or -sulphonic acid chloride,<br>2,3-Dichloroquinoxalinecarboxylic acid chloride or -sulphonic acid chloride,  | 15 |
| 20 | 2,4-Dichloroquinazolinecarboxylic acid chloride or -sulphonic acid chloride,<br>2-Methanesulphonyl-4-chloro-6-methylpyrimidine,<br>Tetrachloropyridazine,<br>2,4-Bis-methanesulphonyl-6-methylpyrimidine,<br>2,4,6-Tri- or 2,4,5,6-tetrachloropyrimidine,   | 20 |
| 25 | 2,4,6-Tri- or 2,4,5,6-tetrabromopyrimidine,<br>2-Methanesulphonyl-4,5-dichloro-6-methylpyrimidine,<br>2,4-Dichloropyrimidine-5-sulphonic acid,<br>5-Nitro- or 5-cyano-2,4,6-trichloropyrimidine,  | 25 |
| 30 | 2,6-Bis-methanesulphonylpyridine-4-carboxylic acid chloride,<br>2,4-Dichloro-5-chloromethyl-6-methyl-pyrimidine,<br>2,4-Dibromo-5-bromomethyl-6-methyl-pyrimidine,<br>2,4-Dichloro-5-chloromethylpyrimidine,<br>2,4-Dibromo-5-bromomethylpyrimidine,  | 30 |
| 35 | 2,5,6-Trichloro-4-methylpyrimidine,<br>2,6-Dichloro-4-trichloromethylpyrimidine or, in particular<br>2,4-Bismethylsulphonyl-5-chloro-6-methylpyrimidine,<br>2,4,6-Trimethylsulphonyl-1,3,5-triazine,<br>2,4-Dichloropyrimidine,<br>3,6-Dichloropyridazine,  | 35 |
| 40 | 3,6-Dichloropyridazine-5-carboxylic acid chloride,<br>2,6-Dichloro- or 2,6-dibromo-4-carboethoxypyrimidine,<br>2,4,5-Trichloropyrimidine,<br>2,4-Dichloropyrimidine-6-carboxylic acid chloride,<br>2,4-Dichloropyrimidine-5-carboxylic acid chloride,   | 40 |
| 45 | 2,6-Dichloro- or 2,6-dibromopyrimidine-4- or -5-carboxylic acid or -sulphonic acid<br>amides or -4- or -5-sulphonic acid chloride,<br>2,4,5,6-Tetrachloropyridazine,<br>5-Bromo-2,4,6-trichloropyrimidine,<br>5-Acetyl-2,4,6-trichloropyrimidine,   | 45 |
| 50 | 5-Nitro-6-methyl-2,4-dichloropyrimidine,<br>2-Chlorobenzthiazole-6-carboxylic acid chloride,<br>2-Chlorobenzthiazole-6-sulphonic acid chloride,<br>5-Nitro-6-methyl-2,4-dichloropyrimidine,<br>2,4,6-Trichloro-5-bromopyrimidine,   | 50 |
| 55 | 2,4,5,6-Tetrafluoropyrimidine,<br>4,6-Difluoro-5-chloropyrimidine,<br>2,4,6-Trifluoro-5-chloropyrimidine,<br>2,4,5-Trifluoropyrimidine,<br>2,4,6-Trichloro- (-tribromo- or -trifluoro)-1,3,5-triazines, and 4,6-dichloro (dibromo-<br>or -difluoro)-1,3,5-triazines which are substituted in the 2-position by an aryl or alkyl<br>radical, for example a phenyl, methyl or ethyl radical, or by the radical of an aliphatic<br>or aromatic mercapto compound bonded via the sulphur atom, or by the radical of an<br>aliphatic or aromatic hydroxy compound bonded via the oxygen atom, or, in particular,<br>by an NH <sub>2</sub> group or by the radical of an aliphatic, heterocyclic or aromatic amino<br>compound bonded via the nitrogen atom. As such compounds, the radicals of which | 55 |
| 60 |   | 60 |
| 65 |   | 65 |

can be bonded in the 2-position to the triazine nucleus by reaction with trihalogenotriazines, include the following: aliphatic or aromatic mercapto or hydroxy compounds, such as thioalcohols, thioglycolic acid, thiophenols, alkoxyalkanols, methyl alcohol, ethyl alcohol or isopropyl alcohol, glycollic acid, phenol, chlorophenols or nitrophenols, phenolcarboxylic and phenolsulphonic acids, naphthols and naphtholsulphonic acids, in particular ammonia and compounds containing amino groups which can be acylated, such as hydroxylamine, hydrazine, phenylhydrazine, phenylhydrazinesulphonic acids, glycol monoalkyl ethers, methylamine, ethylamine, isopropylamine, methoxyethylamine, methoxypropylamine, dimethylamine, diethylamine, methylphenylamine, ethylene-phenylamine, chloroethylamine, ethanolamines, propanolamines, benzylamine, cyclohexylamine, morpholine, piperidine, piperazine, aminocarbonic acid esters, aminoacetic acid ethyl ester, aminoethane-sulphonic acid, N-methylaminoethanesulphonic acid, but, above all, aromatic amines, such as aniline, N-methylaniline, toluidines, xylydines, chloroanilines, *p*- or *m*-aminoacetanilide, aminophenols, anisidine, phenetidine and, in particular, anilines containing acid groups, sulphanilic acid, methanilic acid, orthanilic acid, anilinedisulphonic acid, aminobenzylsulphonic acid, aniline- $\omega$ -methanesulphonic acid, aminobenzenedicarboxylic acids, naphthylaminomonosulphonic, -disulphonic and -trisulphonic acids, aminobenzoic acids, such as 2-hydroxy-5-aminobenzoic acid, and in addition also coloured compounds, or compounds with dyestuff character, for example 4-nitro-4'-aminostilbenedisulphonic acid, 2-nitro-4'-amino-diphenylamino-4,3'-stilbene-disulphonic acid, 2-nitro-4'-aminodiphenylamine-4,3'-disulphonic acid and, in particular, aminoazo dyestuffs or aminoanthraquinones or phthalocyanines which still contain at least one reactive amino group.

The introduction of the substituent in the 2-position of the triazine radical can also be effected after the condensation with the starting diamine or after the reaction, according to the invention, to give the azo dyestuff of the formula (1).

In addition to the fibre-reactive radicals which can be introduced by acylation, further such radicals which may be mentioned are, for example, the vinylsulphone, the  $\beta$ -sulphato- or -thiosulphatoethylsulphone,  $\beta$ -thiosulphatopropionylamide, the  $\beta$ -thiosulphatoethylsulphonylamide or the sulphonic acid-N, $\beta$ -sulphatoethylamide groups, which can be introduced into the diazo component in another way, for example by ester formation or thioester formation.

As compounds which contain a fibre-reactive radical which cannot be introduced by acylation, and in which the fibre-reactive radical is thus preferably not bonded via an amino group, but is bonded directly to the benzene radical, the sulpho esters of the following sulphones may, in particular, be mentioned:

- 1-Amino-2-methoxy-5-( $\beta$ -hydroxyethyl)-phenylsulphone,
- 1-Aminobenzene-3- or -4- $\beta$ -hydroxyethylsulphone,
- 1-Amino-2-methyl-benzene-5- $\beta$ -hydroxyethylsulphone,
- 1-Amino-4-( $\beta$ -hydroxyethylsulphonylpropionylaminomethyl)-benzene,
- 1-Amino-4-( $\beta$ -hydroxyethylsulphonylamino)-benzene,

as well as reactive compounds which can be obtained via the appropriate methylols by Einhorn's method, such as, for example, 1-amino-4-chloroacetylaminomethyl-benzene or 1-amino-3-chloroacetylaminomethyl-benzene-6-sulphonic acid.

The condensation with the acid halides or anhydrides, or with the heterocyclic halogen compounds, is advantageously carried out in the presence of acid-binding agents, such as, for example, sodium carbonate. Of course, all these reactions should be carried out in such a manner that an unsaturated bond or a replaceable halogen atom still remains in the end product.

The azo dyestuffs of the present invention as well as their heavy metal complexes are suitable for dyeing and printing widely different types of materials, particularly textile materials, such as, for example, silk, leather, wool, synthetic fibres of polyamides and polyurethanes, polyester fibres or polyacrylonitrile fibres, and polyhydroxylic materials, such as, for example, cellulose-containing materials of fibrous structure, such as linen, cellulose, regenerated cellulose and cotton.

The non-metallised azo compounds according to the invention are particularly important as dyestuffs.

However, the most important compounds are those azo dyestuffs according to the invention which contain a fibre-reactive radical and a group which confers solubility in water, in particular a sulphonic acid group. These dyestuffs are preferably employed for dyeing nitrogen-containing fibres, such as, for example, of polyamides, polyurethanes, silk, leather and in particular wool, for example from weakly acid, neutral or weakly alkaline baths, optionally with the addition of customary auxiliaries, for example ethylene oxide condensation products of high molecular weight amines, and, above all, for dyeing cellulose materials, in particular cotton, for example by the exhaustion process



from a dilute liquor, from alkaline baths optionally having a high salt content, and in particular by the pad-dyeing process, according to which the article is impregnated with aqueous dyestuff solutions which optionally also contain salt, and the dyestuffs are fixed after an alkali treatment or in the presence of alkali, optionally under the action of heat.

The water-soluble reactive dyestuffs according to the invention show an excellent build-up capacity. They are also suitable for printing, in particular on cotton, and also for printing nitrogen-containing fibres, for example of wool, silk or mixed fabrics containing wool.

The dyeings and printings are generally distinguished by interesting and valuable greenish-tinged yellow, very pure and brilliant shades. The dyeings and printings exhibit good stability to acids and alkalis, and good stability to synthetic resin finishing agents, have a good fastness to light and, in particular on cotton, an outstanding fastness to wet treatments. The high degree of fixation and the easy removability of non-fixed dyestuff is also worth mentioning.

In order to improve the fastness to wet treatments, it is advisable to rinse the dyeings and printings obtained thoroughly with cold and hot water, optionally with the addition of an agent which has a dispersing effect and promotes the diffusion of the non-fixed material.

In the Examples which follow, and which further illustrate the present invention, the parts, unless otherwise indicated, denote parts by weight, and the percentages denote percentages by weight. The relationship of parts by weight to parts by volume is the same as of the gram to the cm<sup>3</sup>.

#### Example 1.

A solution of 18.5 parts of cyanuric chloride in 50 parts of acetone is added to a neutral solution of 26.8 parts of 1,3-diaminobenzene-4,6-disulphonic acid in 500 parts of water at 0 to 5°C, and the pH-value is kept at between 6 and 7 during the condensation by adding, dropwise, 2 N sodium hydroxide solution. When condensation is complete, the resulting monocondensation product is diazotised at 0 to 5°C in the customary manner. A neutral solution of 15.3 parts of 1-ethyl-6-hydroxy-4-methylpyridone(2) is then added to the solution of the diazonium salt. The coupling mixture is adjusted, over the course of about 1 hour, to a pH of 7 by adding 2 N sodium hydroxide solution. The solution of the dichlorotriazine dyestuff is then treated with a neutral solution of 17.3 parts of 1-aminobenzene-3-sulphonic acid and warmed to 40 to 45°C, the pH being kept at between 6 and 7 by adding 2 N sodium hydroxide solution dropwise. The dyestuff formed is isolated by sprinkling sodium chloride into the mixture, and is filtered off and dried. The product dyes cotton in very pure, strongly greenish-tinged yellow shades. An identical dyestuff is also obtained if the primary monocondensation product of 1,3-diaminobenzene-4,6-disulphonic acid and cyanuric chloride is firstly condensed with 1-aminobenzene-3-sulphonic acid, and subsequently coupled to 1-ethyl-6-hydroxy-4-methylpyridone(2).

The manufacture of the coupling component 1-ethyl-6-hydroxy-4-methylpyridone(2) is carried out by boiling 1-ethyl-6-hydroxy-4-methylpyridone(2)-3-carbonamide for several hours with approximately 20% strength sodium hydroxide solution, and subsequently acidifying with hydrochloric acid, whereupon the decarboxylated product of melting point 134—136°C precipitates in a crystalline form.

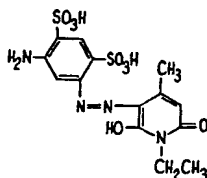
1-Ethyl-6-hydroxy-4-methylpyridone(2) is obtained by heating 1-ethyl-3-cyano-4-methyl-6-hydroxypyridone(2) in aqueous 75% strength sulphuric acid solution at 130°C until the evolution of carbon dioxide is complete.

If the amines indicated in the second column in the following table are employed instead of 1-aminobenzene-3-sulphonic acid (to replace one chlorine atom in the dichlorotriazine dyestuff), and the pyridones specified in the third column in the table are employed instead of 1-ethyl-6-hydroxy-4-methylpyridone(2), further yellow dyestuffs having good fastness properties are obtained.

|    | Amines   | Pyridones   |
|----|--|---|
| 1  | 3-Aminobenzoic acid                              | 1-Methyl-4-phenyl-6-hydroxy-pyridone-2                      |
| 2  | 4-Aminobenzoic acid                              | 1-Isopropyl-4-methyl-6-hydroxy-pyridone-2                   |
| 3  | 1-Aminobenzene-3-methanesulphonic acid           | 1-( $\beta$ -Acetylaminoethyl)-4-methyl-6-hydroxypyridone-2 |
| 4  | 2-Amino-5-sulphobenzoic acid                     | 1-Benzyl-4-methyl-6-hydroxy-pyridone-2                      |
| 5  | N-Methylaniline-4-sulphonic acid                 | 1,4-Diethyl-6-hydroxypyridone-2                             |
| 6  | Aniline-2,4-disulphonic acid                     | 1-Butyl-4-ethyl-6-hydroxy-pyridone-2                        |
| 7  | Anthranilic acid $\omega$ -methanesulphonic acid | 1-Ethyl-4-methyl-6-hydroxy-pyridone-2                       |
| 8  | Aminomethanesulphonic acid                       | 1-( $\beta$ -Phenoxyethyl)-4-methyl-6-hydroxypyridone-2     |
| 9  | Aniline  | 1-Methyl-4-butyl-6-hydroxy-pyridone-2                       |
| 10 | Dimethylamine                                    | 1-Cyclohexyl-4-methyl-6-hydroxypyridone-2                   |
| 11 | Diethanolamine                                   | 1-Ethyl-4-methyl-6-hydroxy-pyridone-2                       |
| 12 | Methylamine                                      | 1-Methyl-4-(4'-methoxyphenyl)-6-hydroxypyridone-2           |
| 13 | Methyltaurine                                    | 1,4-Dimethyl-6-hydroxy-pyridone-2                           |
| 14 | Morpholine                                       | 1-Ethyl-4-methyl-6-hydroxy-pyridone-2                       |
| 15 | Ammonia  | 1-Ethyl-4-methyl-6-hydroxy-pyridone-2                       |
| 16 | 1-Aminobenzene-2-sulphonic acid                  | 1-( $\gamma$ -Hydroxypropyl)-4-benzyl-6-hydroxypyridone-2   |
| 17 | 2-Aminotoluene-4-sulphonic acid                  | 1,4-Diisopropyl-6-hydroxy-pyridone-2                        |
| 18 | 1-Naphthylamine-5-sulphonic acid                 | 1-( $\beta$ -Chloroethyl)-4-ethyl-6-hydroxypyridone-2       |
| 19 | 1-Naphthylamine-4,6-disulphonic acid             | 1-(2',3'-Dihydroxypropyl)-4-methyl-6-hydroxypyridone-2      |
| 20 | 1-Naphthylamine-3,5,7-trisulphonic acid          | 1,4-Diethyl-6-hydroxy-pyridone-2                            |

## Example 2.

47.4 parts of the aminoazo dyestuff of the formula



(manufactured by coupling 31 parts of 1-amino-3-acetylaminobenzene-4,6-disulphonic acid with 15.3 parts of 1-ethyl-6-hydroxy-4-methyl-pyridone-(2) and subsequently saponifying the acetyl amino group with 2 N hydrochloric acid), are dissolved neutral in 500 parts of water, and a solution of 18.5 parts of cyanuric chloride in 50 parts of acetone is added. The pH-value during the condensation is kept between 6 and 7 by adding 2 N sodium hydroxide solution dropwise. When condensation is complete the dichlorotriazine dyestuff is salted out, filtered off and mixed with a concentrated solution of 5 parts of disodium phosphate and 5 parts of monosodium phosphate, and dried in vacuo at 40 to 50°C.

The dyestuff thus obtained dyes cotton in very pure, strongly greenish-tinged yellow shades.

Similar yellow dyestuffs are obtained if, instead of cyanuric chloride, equivalent amounts of  $\alpha,\beta$ -dibromopropionyl chloride, chloroacetyl chloride,  $\alpha$ -bromoacryloyl chloride, 4,5-dichloropyridazonepropionyl chloride, 2,3-dichloroquinoxalinecarboxylic acid chloride, 2,4,5,6-tetrachloropyrimidine, 2,4,6-trifluoro-5-chloropyrimidine, 2,4-bis-methylsulphonyl - 5 - chloro - 6 - methylpyrimidine, 2,4 - dichloro - pyrimidine-5 - carboxylic acid chloride, 3,6 - dichloropyridazine - 5 - carboxylic acid chloride, 2,4 - dichloro - 6 - methyl - 1,3,5 - triazine, 2,4 - dichloro - 6 - phenoxy - 1,3,5-triazine, 2 - amino - 4,6 - dichlorotriazine, cyanuric bromide or 2-methoxy-4,6-dichloro-1,3,5-triazine, are employed.

## Example 3.

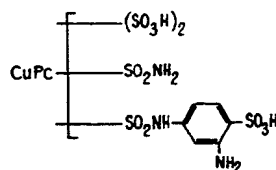
23 parts of 2-isopropoxy-4,6-dichloro-1,3,5-triazine are added to a neutral solution of 26.8 parts of 1,3-diaminobenzene-4,6-disulphonic acid in 500 parts of water, and the reaction mixture is warmed to 40 to 45°C. The pH-value is kept at between 6 and 7 during the condensation by adding 1 N sodium hydroxide solution dropwise. When condensation is complete, the compound thus obtained is diazotised in the customary manner by adding 25 parts of 4 N sodium nitrite solution and 25 parts of 30% strength hydrochloric acid. The pure yellow suspension of the diazonium salt is then treated with a neutral solution of 15.3 parts of 1-ethyl-6-hydroxy-4-methyl-pyridone-(2). The coupling mixture is neutralised by adding 2 N sodium hydroxide solution dropwise. The dyestuff formed is then salted out with potassium chloride, filtered off and dried. The product dyes cotton in very pure, strongly greenish-tinged yellow shades.

If the appropriate amount of 1-methyl-6-hydroxy-4-methylpyridone(2) is used as the coupling component, a dyestuff having very similar properties is obtained.

## Example 4.

The procedure of Example 2 is followed, but a solution of 53 parts of the disodium salt of 1-amino-4-(4'-aminophenylamino)-anthraquinone-2,3'-disulphonic acid in 600 parts of water is added when the condensation is complete, and the temperature is raised to 40—50°C and a pH-value of 6—7 is maintained up to the end of the condensation, by adding sodium hydroxide solution dropwise. The dyestuff formed is precipitated by adding sodium chloride. It dyes cotton in fast, green shades.

If a phthalocyanine dyestuff of the formula



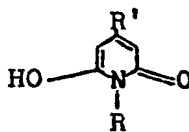
(CuPc = radical of copper phthalocyanine)

is used instead of the aminoanthraquinone mentioned, a green dyestuff is also obtained.

## Example 5.

11 parts of 2-amino-5-sulphobenzoic acid are diazotised in the customary manner. The resulting diazo solution is run into a solution of 7.6 parts of 1-ethyl-4-methyl-6-hydroxypyridone-2 in 500 parts of water at 0°C and 5 parts of 30% strength sodium hydroxide solution, whereupon an intensely yellow dyestuff is immediately formed, which is precipitated completely by adding sodium chloride. It dyes wool from an acid bath in pure greenish-tinged yellow shades. A brownish-tinged yellow colouration is obtained by subsequent chromation.

If the diazo components specified in column II in the following Table are employed instead of 2-amino-5-sulphobenzoic acid, and the pyridones mentioned in column III are employed instead of 1-ethyl-4-methyl-6-hydroxy-pyridone-2 as coupling components, further dyestuffs are obtained which produce dyeings of the shades specified in column IV.

| No. | Diazo Component<br><br>(Nos. 7 and 8 are<br>tetrazo components). | Coupling Component   |           | Shade on<br>Polyamide<br>Fibre<br>Material |
|-----|--|--|-----------|--|
|     |  |  |           |  |
|     |  | R  | R'        |  |
| 1   | 2-Aminobenzene-sulphonic acid                                    | Methyl   | Methyl    | greenish-tinged yellow                     |
| 2   | Naphthylamine-1-sulphonic acid                                   | $\beta$ -Hydroxy-ethyl   | n-Hexyl   | yellow                                     |
| 3   | 4-Aminobenzene-sulphonic acid                                    | Isopropyl  | Methyl    | greenish-tinged yellow                     |
| 4   | 4-(6',8'-Disulphonaphth-2'-ylazo)-3-methylaniline                | Benzyl   | Methyl    | orange                                     |
| 5   | 6-Acetylamino-2-aminophenol-4-sulphonic acid                     | Ethyl  | Isopropyl | yellow-brown<br>(Cu-complex)               |
| 6   | 2-Aminophenol-4,6-disulphonic acid                               | Butyl  | Methyl    | yellow-brown<br>(Co-complex)               |
| 7   | 4,4'-Diaminodiphenyl-urea-3,3'-di-sulphonic acid                 | Ethyl  | Methyl    | reddish-tinged yellow                      |
| 8   | 4,4'-Diaminostilbene-2,2'-disulphonic acid                       | n-Propyl   | Phenyl    | yellow                                     |
| 9   | 2-Aminobenzene-sulphonic acid                                    | Chloro-acetyl-amino-ethyl  | Methyl    | yellow                                     |

## Example 6.

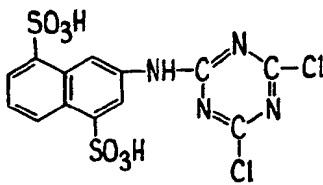
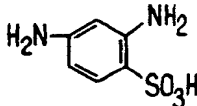
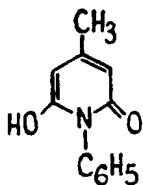
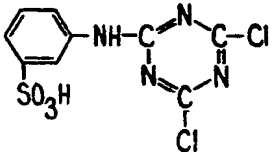
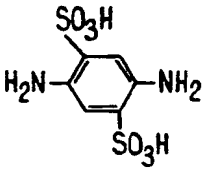
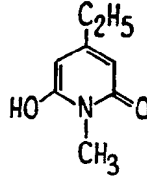
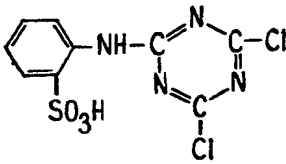

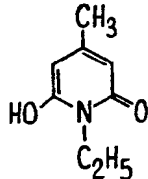
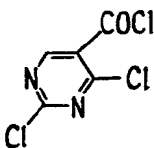
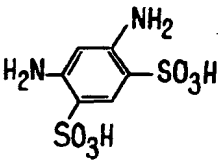
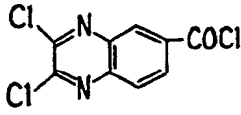
A solution of 25.3 parts of aniline-2,5-disulphonic acid neutralised with sodium carbonate is added to a suspension of 19 parts of cyanuric chloride in 200 parts of ice water. The mixture is kept weakly acid to Congo Red by means of dilute sodium hydroxide solution, and is stirred at a temperature of 8°C until the compounds have completely dissolved. A neutral solution of 18.8 parts of 1,3-diaminobenzene-4-sulphonic acid is then added. The mixture is warmed to 30°C and is slowly neutralised with a solution of sodium hydroxide. When condensation is complete, diazotisation is effected in the customary manner with hydrochloric acid and sodium nitrite. A weakly alkaline solution of 15.3 parts of 1-ethyl-6-hydroxy-4-methylpyridone-(2) is added to the diazo compound, and the coupling mixture is kept weakly acid to neutral by adding 2 N sodium hydroxide solution. The dyestuff is precipitated by adding sodium chloride, and is filtered off and dried. It dyes cellulose fibres in very pure, strongly greenish-tinged yellow shades.

If the same amount of aniline-2,4-disulphonic acid or appropriate amounts of sulphanilic acid, metanilic acid or anthranilic acid, or mixtures thereof, are employed instead of aniline-2,5-disulphonic acid, yellow dyestuffs are obtained which have similar properties to the above-mentioned dyestuff.

If 1-ethyl-6-hydroxy-4-methylpyridone-(2) is replaced by 1,4-dimethyl-6-hydroxy-pyridone-(2), a greenish-tinged yellow dyestuff having good fastness properties is obtained.

Further yellow dyestuffs are obtained according to Example 6, from the components mentioned in the following Table.

|   | I<br>Acyating Agent | II<br>Diazo Component | III<br>Coupling Component |
|---|---------------------|-----------------------|---------------------------|
| 1 |                     |                       |                           |
| 2 |                     |                       |                           |
| 3 |                     | "                     | "                         |
| 4 |                     |                       |                           |

|   | I<br>Acyating Agent   | II<br>Diazo Component  | III<br>Coupling Component  |
|---|---|--|--|
| 5 |    |    |   |
| 6 |    |    |   |
| 7 |   |   |  |
| 8 |  |  | "  |
| 9 |  | "  | "  |

## Example 7.

A weakly alkaline solution of 16.8 parts of 1-( $\beta$ -aminoethyl)-6-hydroxy-4-methylpyridone-(2) (obtained by dissolving in water, with the addition of sodium hydroxide solution) is added to the diazo compound obtained from 25.3 parts of aniline-2,5-disulphonic acid, and the coupling mixture is made neutral with sodium carbonate. When coupling is complete, a solution of 32.2 parts of 2-phenylamino-4,6-dichlorotriazine-3'-sulphonic acid is added and condensation is carried out for 2 hours at 30 to 40°C, the pH-value being kept between 6 and 7 by adding 2 N sodium hydroxide solution dropwise. The dyestuff formed is then salted out, filtered off and dried. It dyes cotton in fast greenish-tinged yellow shades.

5

5

10

10

The pyridone employed as coupling component is obtained by heating 1-( $\beta$ -aminoethyl)-3-cyano-4-methyl-6-hydroxy-pyridone-(2) in aqueous 75% strength sulphuric acid until the evolution of CO<sub>2</sub> is complete.

Similar yellow dyestuffs are obtained if equivalent amounts of the following diazo components are employed instead of aniline-2,5-disulphonic acid:

|   | Diazo Component  | Colour Shade on Cotton |
|---|--|------------------------|
| 1 | 6-Chloro-2-aminophenol-4-sulphonic acid                | reddish-tinged yellow  |
| 2 | 5-Sulphoanthranilic acid                               | yellow                 |
| 3 | 4-(6',8'-Disulphonaphth-2'-ylazo)-2,5-dimethoxyaniline | orange                 |
| 4 | 2-Naphthylamine-1,5-disulphonic acid                   | yellow                 |
| 5 | 2-Naphthylamine-3,6,8-trisulphonic acid                | yellow                 |
| 6 | 1-Amino-4-( $\beta$ -sulphatoethyl-sulphonyl)-benzene  | yellow                 |
| 7 | 1-Amino-4( $\beta$ -sulphatoethylsulphonamide)-benzene | yellow                 |
| 8 | 1-Amino-4-( $\beta$ -hydroxyethyl-sulphonyl)-benzene   | yellow                 |

#### Example 8.

53 parts of the dichlorotriazine dyestuff obtained according to Example 2 are dissolved in 1000 parts of water at a pH of 7. A solution of 5.4 parts of 1,4-phenylenediamine is added and the condensation is carried out at 40—50°C, a pH-value of 6—7 being maintained by adding 2 N sodium hydroxide solution. When condensation is complete, the bireactive dyestuff, in which the two reactive groups are linked by a phenylenediamine bridge, is precipitated by adding sodium chloride. It dyes cotton or regenerated cellulose fibres in pure, strongly greenish-tinged yellow shades.

If an equivalent amount of 1,3-phenylenediamine, 1,4-phenylenediamine-2-sulphonic acid, 4,4'-diaminostilbene-2,2'-disulphonic acid, 4,4'-diaminodiphenyl-2,2'-disulphonic acid or 4,4'-diaminodiphenylurea-3,3'-disulphonic acid is employed instead of 1,4-phenylenediamine, as the bridging component, dyestuffs having similar properties are obtained.

#### Example 9.

17.3 parts of 1-aminobenzene-3-sulphonic acid are dissolved in water, the solution being made neutral by adding sodium hydroxide solution, and are condensed with 18.5 parts of cyanuric chloride in the customary manner at 0—5°C. When condensation is complete, an aqueous solution of 21 parts of the sodium salt of 1,3-phenylenediamine-4-sulphonic acid is added and condensation is carried out at 25—30°C. Thereafter the mixture is cooled to 0°C, 18.5 parts of cyanuric chloride are added, and condensation is carried out at a pH of 4—6 by adding 2 N sodium hydroxide solution dropwise. A further 21 parts of the sodium salt of 1,3-phenylenediamine-4-sulphonic acid are now added, the temperature is raised to 30°C and condensation is carried out at a pH of 6—7. The resulting solution is cooled to 0°C by adding ice, is acidified with 25 parts by volume of 30% strength hydrochloric acid, and is diazotised by adding 4 N sodium nitrite solution dropwise, until a permanent blue colouration is obtained on potassium iodide starch paper.

A solution of 14 parts of 1-ethyl-4-methyl-6-hydroxy-pyridone-2 in 50 parts of water, and 9.5 parts of 30% strength sodium hydroxide solution, are added to the yellow diazo solution. When coupling is complete, the mixture is neutralised to a pH of 7 by adding sodium bicarbonate, and the dyestuff is precipitated by sprinkling in potassium chloride. It dyes cotton in fast greenish-tinged yellow shades.

#### Example 10.

12.6 parts of 6-acetylamino-2-aminophenol-4-sulphonic acid are suspended at 0°C in a mixture of 100 parts of water and 15 parts of 30% strength hydrochloric acid, and diazotised by adding 25 parts of 2 N sodium nitrite solution dropwise. The resulting diazo suspension is added to a solution of 7.7 parts of 1-ethyl-4-methyl-6-hydroxypyridone-2 in 50 parts of water, 50 parts of ice and 5.5 parts of 30% strength sodium hydroxide solution, and the pH is slowly adjusted to 7 by adding sodium hydroxide solution dropwise. When coupling is complete, 30 parts of 36% strength hydrochloric acid are added and the mixture is boiled under reflux for 1 hour to saponify the acetyl group. The dyestuff which crystallises out on cooling is filtered off, is dissolved in 250 parts of water at a pH of 7, and is treated with a solution of 13 parts of cobalt acetate tetrahydrate. The mixture is boiled under reflux for 20 minutes, is then allowed to cool, and the cobalt complex is precipitated by adding sodium chloride. It is dissolved in 500 parts of water at 35—40°C and is treated with an aqueous solution of 16.1 parts of 2-phenylamino-4,6-dichlorotriazine-3'-sulphonic acid. Condensation is carried out at 35—40°C, a pH-value of 6—7 being maintained by adding 2 N sodium hydroxide solution dropwise.

When condensation is complete, the dyestuff is precipitated by adding potassium chloride. It dyes cellulose fibre material in red-orange, fast shades.

If an equivalent amount of chromium acetate is employed instead of cobalt acetate, a dyestuff is obtained which dyes cellulose fibres in fast, red-brown shades.

#### Dyeing Instruction I.

2 parts of the dyestuff of Example 1, 1st. paragraph, are dissolved in 100 parts of water.

A cotton fabric is impregnated on a padder with this solution, and the excess liquid is squeezed out so that the material retains 75% of its weight of dyestuff solution.

The article thus impregnated is dried, then impregnated at room temperature in a solution which contains, per litre, 10 g of sodium hydroxide and 300 g of sodium chloride, squeezed out to 75% liquid uptake, and steamed at 100 to 101°C for 60 seconds. The article is then rinsed, soaped at the boil for quarter of an hour in a 0.3% strength solution of an ion-free detergent, rinsed and dried.

A fixed dyeing which is fast to boiling is obtained. If a cellulose fabric is used instead of a cotton fabric, a similarly good result is obtained.

#### Printing Instruction:

2 parts of the dyestuff obtained according to Example 2 are mixed with 20 parts of urea, dissolved in 28 parts of water, and stirred into 40 parts of a 5% strength sodium alginate thickener. 10 parts of a 10% strength sodium carbonate solution are then added.

A cotton fabric is printed on a roller printing machine using this printing ink, is dried, and the print obtained is steamed at 105°C for 8 minutes. The printed fabric is then thoroughly rinsed in cold and hot water and dried.

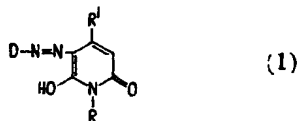
#### Dyeing Instruction II

1 part of the dyestuff according to the first Example of the Table of Example 1 and 3 parts of 80% strength acetic acid are dissolved in 4000 parts of water. 100 parts of polyamide fabric are introduced into this bath at 40°C, the temperature is raised to 96—98°C over the course of 30 minutes, and the fabric is dyed for 60 minutes at the temperature indicated. The dyeing is subsequently well rinsed. A strong, greenish-tinged yellow dyeing is obtained.

#### WHAT WE CLAIM IS:—

1. An azo dyestuff which contains an acid substituent which confers solubility in water, of the formula:





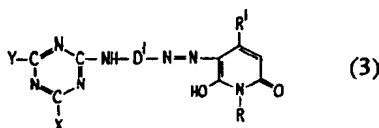
wherein D denotes the radical of a diazo component, R denotes an optionally substituted alkyl or cyclohexyl radical and R' denotes an optionally substituted alkyl or aryl radical.

5        2. An azo dyestuff according to claim 1 wherein R and R' each independently denotes an alkyl radical with 1 to 4 carbon atoms and D denotes the radical of a diazo component of the benzene series. 5

3. An azo dyestuff according to claim 1 or 2 which contains a fibre reactive radical.

10       4. An azo dyestuff according to claim 3, which contains a fibre reactive radical in the substituents R and/or R'. 10

5. An azo dyestuff according to claim 3, of the formula:



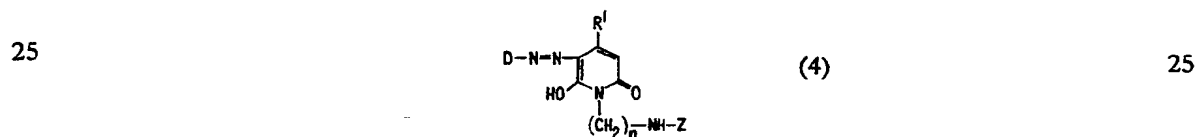
15       wherein D' is a sulphobenzene radical, X is a halogen atom and Y is a halogen atom or an amino, alkoxy, phenoxy or mercapto radical, R and R' are as defined in claim 1, and the benzene radical can contain further substituents. 15

6. An azo dyestuff according to claim 5 in which the benzene radical is substituted by metal complex-forming groups in the *ortho* position to the azo bridge.

20       7. An azo dyestuff according to claim 5 or 6 wherein D' is a monosulphobenzene radical, Y is an aminobenzene (or naphthalene)-disulphonic acid radical, and R and R' are each a methyl or ethyl radical. 20

8. An azo dyestuff according to claim 7, wherein D' contains no further substituents.

9. An azo dyestuff according to Claim 4, of the formula



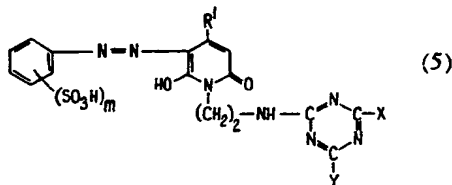
wherein D is the radical of the diazo component of the benzene or naphthalene series, R' is as defined in Claim 1, Z is a fibre reactive radical, and n is a positive integer.

10. An azo dyestuff according to Claim 9, wherein D contains an acid substituent which confers solubility in water.

30       11. An azo dyestuff according to Claims 8 and 9, wherein Z is a dihalogenotriazine radical or a monohalogenotriazine radical which contains an ammonium, amino, alkoxy, phenoxy or mercapto radical, bonded to a carbon atom of the triazine ring. 30

35       12. An azo dyestuff according to any one of claims 9 to 11, wherein n denotes an integer from 1 to 4. 35

13. An azo dyestuff according to Claim 9 of the formula



wherein X is a halogen atom, Y is an aminobenzene (or -naphthalene)-sulphonic acid radical, R' is an alkyl radical of 1 to 4 carbon atoms and m = 1 or 2.

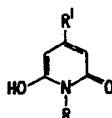
14. An azo dyestuff according to Claim 13, wherein X is a chlorine or bromine atom.

5 15. An azo dyestuff according to Claim 13 or 14, wherein R' is a methyl radical. 5

16. A heavy metal (as hereinbefore defined) complex of an azo dyestuff as claimed in any one of Claims 1 to 7 and 9 to 12.

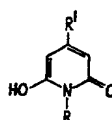
10 17. An azo dyestuff or heavy metal complex thereof according to Claim 1 or 16 specifically identified herein. 10

18. Process for the manufacture of an azo dyestuff as claimed in any one of the preceding claims which comprises coupling a diazo component derived from an amine of the formula: D—NH<sub>2</sub> with a compound of the formula



15 wherein D, R and R' are as defined in Claim 1 and optionally reacting the resulting azo dyestuff with a metallising agent and/or acylating agent. 15

19. Process according to Claim 18 in which a diazo component of the benzene series is coupled with a compound of the formula



(6)

20 wherein R and R' represent alkyl radicals with 1 to 4 carbon atoms. 20

20. Process according to Claim 18 or 19 for the manufacture of an azo dyestuff as claimed in claim 5 in which the radical of the diazo component contains a halogenotriazine group, which is optionally reacted with ammonia or an amine, alcohol, phenol or mercaptan, before or after coupling.

25 21. Process according to Claim 18 in which the azo dyestuff obtained is treated with a metal donor. 25

22. Process according to Claim 18 substantially as hereinbefore described.

23. Process according to claim 18 substantially as described in any one of Examples 1 to 10.

30 24. An azo dyestuff according to claim 1 or 16 whenever manufactured by a process as claimed in any one of claims 18 to 23. 30

25. Process for dyeing or printing a textile material which comprises dyeing or printing it with a dyestuff as claimed in any one of claims 1 to 16 and 24.

35 26. A textile material wherever dyed or printed by a process as claimed in claim 25. 35

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